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Applicant(s): ;

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ABSTRACT:

# PATENT SPECIFICATION

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DRAWINGS ATTACHED

1 204 541

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## (54) METHOD OF MAKING FIBRE REINFORCED PLASTER ARTICLES

(71) We, NATIONAL RESEARCH DEVELOPMENT CORPORATION, a British Corporation established by Statute of Kingsgate House, 66—74, Victoria Street, London, S.W.1., do hereby declare the invention for which we pray that a patent may be granted to us, and the method by which it is to be performed, to be particularly described in and by the following statement:—

10 This invention relates to a method of making fibre-reinforced plastic articles.

According to one aspect of the invention there is provided a method of making a plaster article comprising mixing glass fibres with an aqueous slurry of gypsum plaster to produce a mixture in which the fibres are well dispersed, delivering the mixture to a mould either during or after mixing, and extracting water from the mixture to lower the water/plaster ratio to a value approaching but not below the minimum required to hydrate the plaster.

According to another aspect of the invention a method of making a plaster article comprises impregnating a glass fibre mat with an aqueous slurry of gypsum plaster, transferring the impregnated mat to a mould and extracting water from the impregnated mate to lower the water/plaster ratio to a value approaching but not below the minimum required to hydrate the plaster.

Two or more impregnated glass fibre mats may be superimposed and consolidated in the mould.

35 The extracted water may be extracted from the mixture or the impregnated mat by suction, centrifugal action or pressure, or by any suitable combination of these means.

40 The invention can be used for making glass fibre reinforced gypsum plaster boards, mouldings or extrusions for constructional use, for example, in the manufacture of wall, floor, ceiling or roof structures, doors or cabinets. Such articles can be arranged to have good fireproof characteristics and high

strength, particularly flexural strength and impact strength.

The initial aqueous slurry of gypsum plaster, possessing a relatively high water/plaster ratio, ensures that the glass fibres are well dispersed therein and/or well wetted to ensure a good bond between the fibres and the plaster. The initial water/plaster ratio may be at least fifty parts by weight of water to a hundred parts by weight by plaster.

For the best results in terms of the strength of the article, the water/plaster ratio after extraction of the water should be such that there is just enough water to hydrate the plaster. For example, for a hemihydrate gypsum plaster mix the lower water plaster ratio should be of the order of 18% which will result in a plaster having a compressive dry strength of up to 10,000 p.s.i.

To achieve these best results the extraction of excess water is preferably at least in part effected by pressing the article in the mould. Pressure of the order of 400 lb. p.s.i. is preferably employed. Using pressure to extract excess water has the added advantage that the article being moulded is consolidated.

While, if desired for specific purposes, the glass fibres may be orientated in one direction or another, for general purposes a random distribution gives good results. The glass fibre used is conveniently low-alkali boro-silicate (E glass) which is readily commercially available either in the form of roving, chopped strand, or mat. Good results have been obtained using fibres one to two inches in length. The amount of fibre employed is largely a matter of choice depending upon the strength required. It has been found, however, that if more than about 15% by weight of fibres is added the composite tends to become spongy and cannot be adequately consolidated.

Plaster boards incorporating 10% by weight of glass fibre have been found to have bending strengths (modulus of rupture) of 15,000

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lb. p.s.i. and impact strengths of 400 in lb. p.s.i.

One embodiment of the present invention is further described below with reference to the diagrammatic drawing accompanying the Provisional Specification, in which:—

Figure 1 shows apparatus for impregnating a glass fibre mat with a fluid plaster mix and for removing some of the water from the mix, and

Figure 2 shows a filter press for removing more water from the impregnated mat.

Referring first to Figure 1, a vessel 1 contains a gypsum plaster mix 2 with a relatively high water/plaster ratio. A suction box 3 connected by an outlet tube 4 to a vacuum pump (not shown) has an open bottom located just below the surface of the mix 2. A grill 5 extends across the open bottom.

A glass fibre mat 6 extends through the mix 2 below the suction box 3. In operation, the mix 2 impregnates the mat 6 and some water is removed from the impregnating mix by suction. In a continuous production process, the mat 6 may be drawn through the mix 2 on a permeable belt, or the suction

box 3 may be replaced by a rotating perforated drum.

The filter press shown in Figure 2 includes upper and lower platens 7 with grooves 8 in their opposed surfaces covered by filters 9. In use, the impregnated mat is located between the platens 7 which are then forced towards one another to apply pressure to the mat such that water is expelled from the mat and escapes through the filters 9 and grooves 8.

The following is an example of the type of material that can be produced by such a process.

A mat of chopped E glass rovings, weighing  $1\frac{1}{2}$  oz. per sq. ft. was impregnated on the suction box with a hemihydrate gypsum plaster mix having a water/plaster ratio of 1.0 by weight. Three layers of this impregnated mat were consolidated on the filter press to a water/plaster ratio of 0.23 i.e. 5 per cent in excess of the amount required to hydrate the plaster.

The properties of this board, in the dry state, were as follows:—

|    |  |                     |
|----|--|---------------------|
|    | Thickness  | $\frac{1}{2}$ inch  |
|    | Weight   | 2.9 lb./sq.ft.      |
|    | Glass fibre content  | 10% of total weight |
|    | Flexural strength  | 8,700 p.s.i.        |
| 55 | Impact strength (Izod), greater than 200 in lb./in. <sup>2</sup> |                     |

This material can be compared with asbestos cement, which it somewhat resembles in its method of manufacture and in its possible production in the form of sheets, pipes, moulded products and extrusions.

In comparison with asbestos cement, it has the disadvantage that in common with all gypsum plaster products it can only be used where it is protected from the weather, since gypsum is slightly soluble in water. However, although restricted to internal use it has many compensating advantages, namely:

In manufacture, there is very rapid development of strength and therefore no need for stockpiling.

In use, the flexural strength is more than double that of asbestos cement, and the impact strength is greater by an order of magnitude. Asbestos cement shatters on impact, but this material suffers only slight localised damage. It is suitable for any type of decorative treatment or surface coating, and has very good fire-resistance, since the gypsum plaster contains a considerable proportion of combined water.

In order to make a plaster article in which glass fibres are dispersed rather than provided

in the form of a mat, although they may be mixed with the initial aqueous slurry of gypsum plaster in any suitable manner, for example, by stirring or agitating, a particularly useful method of mixing is simultaneously to spray the slurry and chopped rovings over the surface of a mould. When using this mixing technique the mould is preferably in the form of a vacuum bed comprising for example a perforated steel plate covered with a special high wet-strength paper, the excess water being extracted by suction from below. By this means it is possible to produce curved or folded shapes, or honeycomb structures which will allow the material to be used for folded-plate or stressed skin constructions.

A suction of 12 lb./sq.in. has been found adequate to remove the excess water though to achieve the most efficient dewatering and also better compaction of the composite it is necessary to subject the same to pressure of about 400 lb./sq.in.

Details of a number of glass fibre reinforced composites made by simultaneously spraying the fibres and an aqueous slurry on a mould as described above, and their properties, are set out in the table below:—

| Sample | Plaster               | E glass fibre  |                    |              | Water/Binder      |                    | Density<br>g/ml. | Flexural<br>strength<br>lb/in <sup>2</sup> | Impact<br>strength<br>in.lb/in <sup>2</sup> | Tensile<br>strength<br>lb/in <sup>2</sup> |
|--------|-----------------------|----------------|--------------------|--------------|-------------------|--------------------|------------------|--|---|---|
|        |                       | Length<br>(in) | % by wt. of        |              | Ratio (by weight) |                    |                  |  |   |   |
|        |                       |                | Demoulded<br>panel | Dry<br>panel | Slurry            | Demoulded<br>panel |                  |  |   |   |
| 1      | $\beta$ Hemihydrate   | 2              | 6.5                | 7.4          | 0.49              | 0.34               | 1.45             | 3,630                                      | 171   | 1,650                                     |
| 2      | (Plaster of           | 2              | 9.7                | 11.0         | 0.49              | 0.29               | 1.45             | 2,750                                      | 251   |   |
| 3      | Paris)                | 2              | 9.7                | 11.5         | 0.49              | 0.30               | 1.45             | 3,610                                      | 206   | 1,560                                     |
| 4      |                       | 2              | 12.1               | 14.5         | 0.52              | 0.30               | 1.39             | 3,120                                      | 275   | 1,750                                     |
| 5      |                       | 1              | 10.8               | 12.4         | 0.52              | 0.35               | 1.60             | 4,500                                      | 210   | 2,380                                     |
| 6      |                       | 1½             | 8.4                | 10.1         | 0.49              | 0.30               | 1.48             | 3,880                                      | 133   |   |
| 7      |                       | 2              | 11.4               | 12.5         | 0.52              | 0.18               | 1.70             | 4,260                                      | 232   | 2,060                                     |
| 8      | $\alpha$ -Hemihydrate | 2              | 6.8                | 7.1          | 0.40              | 0.17               | 1.88             | 4,570                                      | 167   | 2,000                                     |
| 9      | (autoclaved)          | 2              | 10.6               | 10.8         | 0.40              | 0.16               | 1.74             | 4,680                                      | 261   | 2,370                                     |
| 10     | plaster               | 2              | 12.3               | 12.6         | 0.40              | 0.18               | 1.77             | 4,490                                      | 282   | 2,450                                     |

NOTE: Sample No. 7 was pressed (at 400 lb/in<sup>2</sup>) after forming on the suction mould.

#### WHAT WE CLAIM IS:—

1. A method of making a plaster article comprising mixing glass fibres with an aqueous slurry of gypsum plaster to produce a mixture in which the fibres are well dispersed, delivering the mixture to a mould either during or after mixing, and extracting water from the mixture to lower the water/plaster ratio to a value approaching but not below the minimum required to hydrate the plaster.

2. A method of making a plaster article comprising impregnating a glass fibre mat

with an aqueous slurry of gypsum plaster, transferring the impregnated mat to a mould and extracting water from the impregnated mat to lower the water/plaster ratio to a value approaching the minimum required to hydrate the plaster.

3. A method as claimed in Claim 2 in which two or more glass fibre mats are impregnated, superimposed and consolidated in the mould.

4. A method as claimed in Claim 1, 2 or 3 in which water is at least in part extracted

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by applying pressure to the mixture or the impregnated material, as the case may be, in the mould.

5 5. A method as claimed in Claim 5 in which a pressure of the order of 400 lb./sq.in. is applied.

10 6. A method as claimed in any one of the preceding claims in which the extracted water is at least initially extracted by applying suction to the mixture or the impregnated mat, as the case may be, in the mould.

15 7. A method as claimed in any one of the preceding claims in which the aqueous slurry of gypsum plaster comprises at least fifty parts by weight of water to a hundred parts by weight of plaster.

20 8. A method as claimed in any one of the preceding claims in which the glass fibre comprises low-alkali boro-silicate (E glass).

9. A method as claimed in Claim 1 or any

of Claims 3—8, as dependant thereon, in which the glass fibre is in the form of roving or chopped strand.

10. A method as claimed in claim 9 in which the glass fibres are one to two inches 25 in length.

11. A method as claimed in claim 9 or 10 in which up to 15% by weight of glass fibres is mixed with the aqueous slurry.

12. A method of making a high strength 30 plaster article substantially as herein described in the example, or with reference to the drawing accompanying the Provisional Specification, or the accompanying table.

13. A plaster article or composite produced 35 by the method claimed in any one of the preceding claims.

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FIG.1.

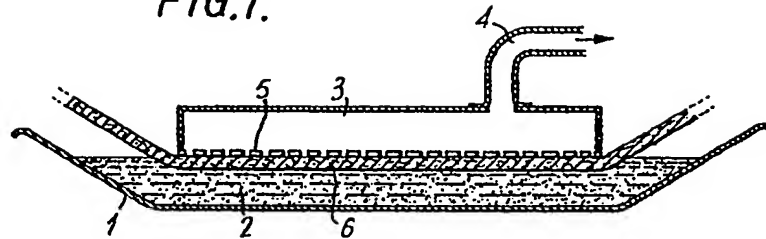
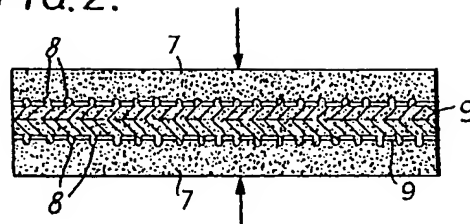


FIG.2.



Requested Patent: GB1520241A

Title:

METHOD FOR BRIGHTENING THE ELECTRODEPOSITS OF ZINC FROM  
ALKALINE ZINC ELECTROPLATING BATHS ;

Abstracted Patent: US4113583 ;

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**ABSTRACT:**

A method for depositing bright zinc from zinc electrodeposition baths in which a compound prepared by reacting imidazole and/or at least one imidazole derivative with at least one organic compound which quaternizes nitrogen in said imidazole in the presence of water is added to the alkaline zinc electroplating baths.

# PATENT SPECIFICATION

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1 520 241

- (21) Application No. 12890/77 (22) Filed 28 March 1977  
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 (33) Japan (JP)  
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 (51) INT CL<sup>2</sup> C25D 3/24  
 (52) Index at acceptance C7B 120 432 450 452 456 461 738 DK



## (54) A BATH FOR THE ELECTRODEPOSITION OF BRIGHT ZINC

(71) We, DIPSOL CO., LTD., a Japanese body corporate, of 4, 3-chome, Kyobashi, Chuo-ku, Tokyo, Japan, do hereby declare the invention, for which we pray that a patent may be granted to us, and the method by which it is to be performed, to be particularly described in and by the following statement:—

This invention relates to alkaline zinc electroplating bath for the deposition of bright zinc.

Various types of brightener additives for alkaline zinc electroplating process such as organic aldehyde compound combining with a substituent, a ketone compound, a heterocyclic compound, a sulfur organic compound and/or a water-soluble high molecular compound have been widely investigated. These brightener additives which have been developed in the prior art are not satisfactory for use in specific alkaline zinc electroplating baths such as zincate or cyanide baths, so far as workability and the plating of zinc at high current density are concerned.

We found that these defects were removed by providing an aqueous alkaline zinc electroplating bath for the deposition of bright zinc, the bath containing a water-soluble brightener prepared by reacting imidazole and/or at least one substituted imidazole with a quaternizing agent comprising at least one organic compound which quaternizes nitrogen in the imidazole or the substituted imidazole(s) in the presence of water.

The starting materials for the preparation of the brightener are thus imidazole and/or one or more substituted imidazoles such as 1 - methylimidazole, 1 - ethylimidazole, 2 - methylimidazole, 1,5 - dimethylimidazole, 1 - ethyl - 2 - methylimidazole, 1 - oxymethylimidazole and/or 1 - vinylimidazole, and suitable quaternizing agents such as monochloroacetic acid, benzyl chloride, chloroacetamide, 3 - aminobenzyl chloride, dichloroglycerine, methyl iodide, allyl chloride, dichloroethane and/or monochloropropane.

The brightener can be prepared by adding at least one quaternizing agent to imidazole and/or at least one substituted imidazole in

quantities ranging from one mole to 1.5 moles per mole of the imidazole(s) and then reacting the materials for from 0.5 to 4 hours at from 40 to 100°C in the presence of such water quantities that the reaction products are dissolved. The brightener thus prepared is preferably added to zincate electroplating baths in ratios of 0.1—3 g/l (considered as an anhydrous compound) or to zinc cyanide electroplating baths in ratios of 0.05—0.5 g/l (considered as an anhydrous compound).

The zinc electrodeposited from such baths exhibits a considerably enhanced brightening effect and they are satisfactory for use at high current density and moreover no "burnt" deposit or pitting is found on the plated zinc.

Brightener additives of the prior art herein-after disclosed can be added to a bath according to the invention, if desired.

Having generally described this invention, a further understanding can be obtained by reference to certain specific examples which are provided herein for purpose of illustration only and are not intended to be limiting unless otherwise specified. The Examples show the preparation of some brighteners for baths according to the present invention and a bright zinc layer electrodeposited by each bath used containing one of the brighteners.

### Examples

Imidazole or 1-ethylimidazole, benzylchloride or monochloroacetic acid and water were added at the following mixing ratios to a four-necked flask equipped with a thermometer, a condenser, a stirrer and a separatory funnel.

| Mixing Ratios |                       |        |
|---------------|-----------------------|--------|
| No. 1         | Imidazole             | 6.8 g  |
|               | Benzyl chloride       | 12.6 g |
|               | Water                 | 10.0 g |
| No. 2         | Imidazole             | 6.8 g  |
|               | Monochloroacetic acid | 9.5 g  |
|               | Water                 | 10.0 g |



No. 3 1-ethylimidazole 8.2 g  
Benzyl chloride 12.6 g  
Water 10.0 g

Bath of low cyanide concentration (L—CN)

Zn 10 g/l  
NaCN 12.5 g/l  
NaOH 70 g/l

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5 The mixture was warmed to 80°C for 1 hour. The reaction products thus prepared were diluted to 100 g with water.

The water solutions thus prepared were added at the various ratios to the zincate electroplating bath and the zinc cyanide electroplating bath of which the compositions are shown as follows:

Zincate bath (Z)

Zn 10 g/l  
NaOH 120 g/l

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Bath of medium cyanide concentration (M—CN)

The electroplating of zinc on steel was performed by passing an electric current at a bath temperature of 25°C. 25

The experimental results are shown in the following table.

15 Zn 20 g/l  
NaCN 40 g/l  
NaOH 80 g/l

| Test Number   | 1         | 2                   | 3         | 4                   | 5                     | 6                   | 7         | 8                        | 9         | 10                       | 11                       |
|---|-----------|---------------------|-----------|---------------------|-----------------------|---------------------|-----------|--------------------------|-----------|--------------------------|--------------------------|
| Kind of Bath  | Z         |                     |           |                     |                       |                     |           |                          |           |                          |                          |
| Kind of Brightener Additive   | L-CN      |                     |           | M-CN                |                       |                     | M-CN      |                          |           | M-CN                     |                          |
|   | No. 1     | Comparative Example | No. 2     | Comparative Example | No. 3                 | Comparative Example | No. 1     | Comparative Example      | No. 2     | Comparative Example      | No. 3                    |
| (g/l)   | 1         | —                   | 0.8       | 0.8                 | —                     | —                   | 0.1       | —                        | 0.05      | —                        | —                        |
| A (g/l)   | 4         | 4                   | —         | —                   | 2                     | 2                   | 0.5       | 0.5                      | —         | —                        | —                        |
| B (g/l)   | —         | —                   | 6         | 6                   | 3                     | 3                   | —         | —                        | —         | —                        | —                        |
| Anisaldehyde (g/l)  | 0.5       | 0.5                 | —         | 0.5                 | —                     | 0.5                 | 0.2       | 0.2                      | 0.1       | 0.1                      | 0.1                      |
| Polyvinyl alcohol (g/l)   | —         | —                   | —         | —                   | —                     | —                   | 0.2       | 0.2                      | 0.2       | 0.2                      | 0.2                      |
| Current Density (A/dm <sup>2</sup> )  | 0.5-6     | 0.5-2               | 0.5-7     | 0.5-7               | 0.5-2                 | 0.5-8               | 0.3-8     | 0.3-3                    | 0.3-8     | 0.3-4                    | 0.3-4                    |
| Brightness of plated Zinc   | Very Good | Good                | Good      | Very Good           | Fairly Good           | Very Good           | Very Good | Good                     | Very Good | Good                     | Good                     |
| Burnt deposit or Pits on plated Zinc (Current Density 4 A/dm <sup>2</sup> ) | Not Found | Found               | Not Found | Not Found           | Found in Large Number | Not Found           | Not Found | Found in a little Number | Not Found | Found in a little Number | Found in a little Number |

The comparative examples in which one kind (A or B) of brightener additive of the prior art was added to the same alkaline electroplating baths in place of the brightener used according to the invention are shown together in the table. The brightener additive A is a 50% water solution of the reaction product of methylamine and epichlorohydrin, and the brightener additive B is a 50% water solution of polyethyleneimine (polymerization degree, about 2000).

Moreover, though the cases in which the brightener additive No. 2 or No. 3 was added in the electroplating bath L—CN, and the cases in which the brightener additive No. 1 or No. 3 was added in the electroplating bath M—CN were not shown in the above table, the same superior results as could be seen from the cases of the electroplating bath Z were obtained in both cases.

#### WHAT WE CLAIM IS:—

1. An aqueous alkaline zinc electroplating bath for the deposition of bright zinc, the bath containing a water-soluble brightener prepared by reacting imidazole and/or at least one substituted imidazole with a quaternizing agent comprising at least one organic compound which quaternizes nitrogen in the imidazole or the substituted imidazole(s) in the presence of water.

2. A bath as claimed in claim 1, the substituted imidazole(s) being selected from the group consisting of 1 - methylimidazole,

1 - ethylimidazole, 2 - methylimidazole, 1,5 - dimethylimidazole, 1 - ethyl - 2 - methylimidazole, 1 - oxymethylimidazole, and 1 - vinylimidazole.

3. A bath as claimed in claim 1 or 2, the quaternizing agent comprising at least one compound selected from the group consisting of monochloroacetic acid, benzyl chloride, chloroacetamide, 3 - amino - benzyl chloride, dichloroglycerine, methyl iodide, allyl chloride, dichloroethane, and monochloropropane.

4. A bath as claimed in any of claims 1 to 3, the quaternizing agent having been added to the imidazole and/or the substituted imidazole(s) in quantities ranging from one mole to 1.5 moles per mole of the imidazole(s).

5. A bath as claimed in claims 1 to 4, the imidazole and/or the substituted imidazole(s) having been allowed to react with the quaternizing agent at 40 to 100°C for 0.5 to 4 hours in the presence of a quantity of water such that the reaction products are dissolved.

6. A bath as claimed in any of claims 1 to 5, being a zincate bath.

7. A bath as claimed in claim 6, containing 0.1 to 3 grams of the brightener per litre.

8. A bath as claimed in any of claims 1 to 5, being a cyanide bath.

9. A bath as claimed in claim 8, containing 0.05 to 0.5 grams of the brightener per litre.

10. A bath as claimed in claim 1, substantially as described herein.

MARKS & CLERK.